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Effect of electron beam radiation dose on the foam formation in pre-ceramic polymer

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ABSTRACT

Methylsilicone resin as a polymer precursor for a SiOC ceramic material was cured and foamed by electron beam (EB) irradiation in air prior to the pyrolysis under an inert atmosphere. Methylsilicone foams were obtained without additional foaming agent when exposed to accelerated electrons with radiation doses up to 9 MGy and dose rate of 2.8 kGy/s. During irradiation the polymer was melted and simultaneously gaseous products were formed by the methyl group oxidation and by the polycondensation crosslinking reactions. The formed gases could not escape from the molten polymer and began to aggregate into bubbles. The effect of the radiation dose on the polymer foam molecular structure, the gel fraction and the ceramic yield was analyzed. The results indicate that the maximum amount of crosslinking in methylsilicone, when EB radiation is used, occurred between 1.0 and 2.0 MGy radiation dose. Methylsilicone foams were pyrolysed in N_2 atmosphere at temperatures of 1200 and 1500 °C, resulting in amorphous SiOC and partially crystalline ceramic foams, respectively. A porosity of ~84% was achieved in the pyrolyzed foams, with cell size ranging from 30 to 300 μm and density of about 0.31 g cm^{-3}.

1. Introduction

For decades, polymers in general have been treated with high energy radiation and industries such as wire and cable insulation rely on this technology (Clough, 2001; Berejka and Eberle, 2002). An advantage of using radiation as a method of curing is that once radiation has ceased, no further reaction takes place and the extent of curing is completely determined by the radiation dose. A further advantage is that the irradiated material itself is purer, without catalysts or foaming agents. However, studies about pre-ceramic polymers treated with radiochemical reactions are very scarce. The few studies in which precursor polymer are cured by electron beam (EB) irradiation are related to the manufacture of non-oxide ceramic fibers. To reduce the oxygen content in the polycarbosilane (PCS) fiber, the conventional method of thermal oxidation curing was substituted by EB radiation curing in an oxygen free atmosphere (Seguchi, 2000). The EB irradiated PCS fibers were converted to silicon carbide (SiC) fibers with very low oxygen content (Idesaki et al., 2001). Also, radiation cured PCS fibers were found to convert to silicon nitride (Si_3N_4) fibers by pyrolysis in NH_3 atmosphere (Kamimura et al., 1999). This technology has already been commercialized and SiC fibers synthesized with this curing method have excellent thermal resistance at temperatures up to 1700 °C (Shimoo et al., 1998).

It has recently been investigated the foaming of a pre-ceramic polymer by electron beam irradiation (Rocha et al., 2008). It was shown that methylsilicone resin foams can be prepared by simultaneous curing and foaming, without the addition of calalysts or blowing agents. These foams were converted to SiOC ceramic foams upon pyrolysis in inert atmosphere exhibiting good compression strength. The aim of this work was to investigate the effect of electron beam radiation dose on the foam formation and reticulation degree in methylsilicone resin in the dose range of 1.0–9.0 MGy, fixing the dose rate at 2.8 kGy/s.

2. Experimental

The pre-ceramic polymer was a commercially available methylsilicone resin with a general formula of $(CH_3SiO_{1.5})_n$ with $n = 130–150$ (MK, Wacker AG, Burghausen, Germany). It is a solid resin in the form of powder at room temperature with density of 1.1 g cm^{-3}, average molecular weight of 9500 g mol^{-1} and has a glass transition temperature of 41.9 °C. According to the manufacturer of this resin and published literature (Wei et al., 2002), the amount of crosslinking active hydroxyl (–Si–OH) and ethoxy ($-Si-OC_2H_5$) functional groups is a few mol percent (~4 mol%) and

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these undergo crosslinking reactions at 150–250 °C, generating water and ethanol as by-products during curing.

The silicone resin powder was compacted in a uniaxial press into pellets of 25 mm in diameter and 2.5 mm thick. The samples were placed in a steel sample holder $500 \times 35 \times 25\,mm^3$ and covered with a thin metal film (0.1 mm thick aluminum foil). To irradiate, the sample holder was placed under an EB in an industrial EB accelerator (Dynamitron II, 1.5 MeV, 25 mA). A set of irradiations were performed with samples being continuously irradiated with doses of 1.0, 2.0, 2.5, 3.0, 3.5, 7.0 and 9.0 MGy. A dose rate of 2.8 kGy/s and current of 0.7 mA were used in air atmosphere without sample holder cooling. The temperature during irradiation was measured by a thermocouple placed on the top of the polymer pellet.

The gel fraction of the irradiated samples was determined gravimetrically by the Soxhlet extraction method and using a compatible solvent (based in ASTM 2765-01). Five samples were tested at each radiation dose. Then, the gel fraction was estimated using Eq. (1):

$$\text{Gel fraction}(\%) = \frac{[\text{mass after extraction}] \times 100}{\text{mass before extraction}} \quad (1)$$

The Fourier transform infrared (FTIR) spectra of the methylsilicone foams were obtained using a Nicolet Nexus spectrometer. A pellet sample was used in the spectrometer and this was prepared by grinding 1 mg of foam, mixed with 150 mg of dried KBr powder and pressed. The spectra were obtained in the wavenumber range 4000–400 cm^{-1}.

Differential thermogravimetric (TG) analysis was carried out in a (Perkin-Elmer, TGA-7) thermal balance in air up to 1000 °C with a constant heating rate of 10 °C/min. The microstructure and morphology of the foams were examined in scanning electron microscope (SEM-Philips XL 30; LEO-435 Pi). The crystalline structures were evaluated by X-ray diffraction (XRD) analysis using Cu Kα radiation (Philips model PW 18/30).

Obtained foams with 7.0 MGy were pyrolyzed in an electric furnace in N_2 atmosphere and at final temperatures of 1200 and 1500 °C with a soaking time of 1 h. The bulk (apparent) density of the foams was calculated from the weight/volume ratio and total porosity of the pyrolyzed foams was determined by Hg intrusion with a high pressure porosimeter (Auto Pore III-Micromeritics).

3. Results and discussion

Foam formation in methylsilicone during EB irradiation was obtained in all range of applied radiation dose. Fig. 1 shows scanning electron micrographs of the fracture surface of methylsilicone resin after EB irradiation with radiation dose of 1.0 MGy (Fig. 1a) and 7.0 MGy (Fig. 1b). It can be noted that both radiation doses promote bubble formation and stabilization, though radiation dose of 1 MGy shows less expansion and foam with smaller cell size. Foam irradiated with 7 MGy (Fig. 1b) shows interconnected porous cells and cell windows covered by a thin membrane. Bulk density of the foam irradiated with 1.0 MGy was $0.65 \pm 0.04\,g\,cm^3$ while foams obtained above 2.0 MGy was $0.20 \pm 0.02\,g\,cm^3$ regardless the applied dose.

In order to analyze foam formation in methylsilicone by radiation crosslinking, the temperature inside the sample holder during irradiation was measured. At 1.0 MGy the temperature increased from room temperature to 210 °C in 6 min. The increase in temperature caused the polymer to melt and its viscosity was adequate for bubble formation and stabilization (Fig. 1b). After this fast heating the temperature increased slowly with increase in radiation dose, until a constant temperature of about 260 °C. At radiation dose of 2.0 MGy, the temperature increased to 230 °C in

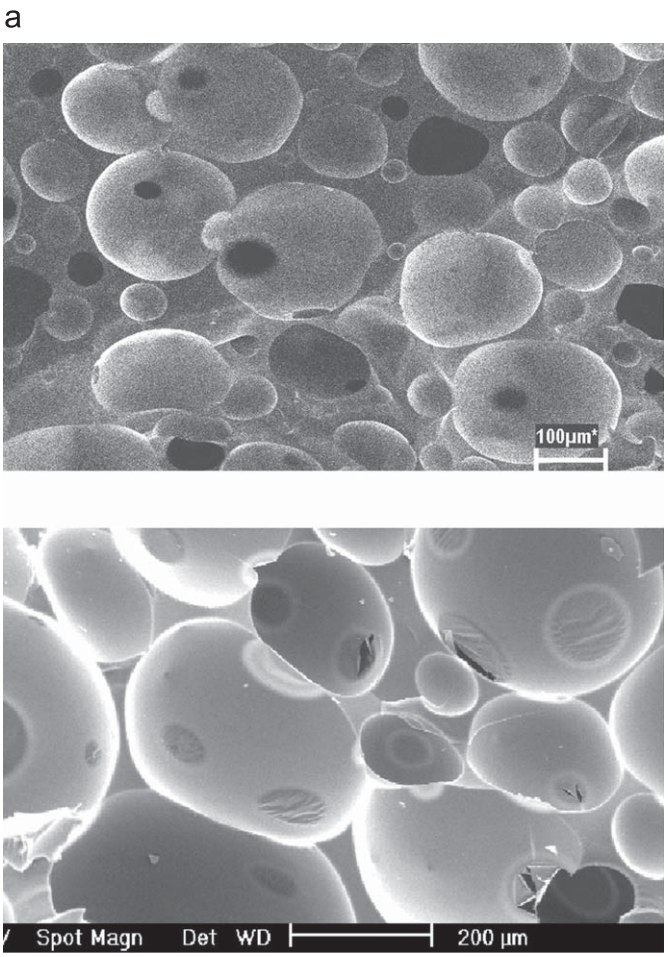

Fig. 1. Scanning electron micrographs of the methylsilicone fracture surface: (a) irradiated with dose of 1.0 MGy; (b) irradiated with dose of 7.0 MGy.

12 min and the polymer viscosity was still appropriate to allow further expansion. Because of the high temperature during irradiation, it could be supposed that crosslinking reactions were activated not only by radiation crosslinking but also by thermal crosslinking. However, when only thermal crosslinking is considered, longer heat treatments are necessary, about 2 h at 200 °C to obtain a totally crosslinked unmelted thermoset foam (Zeschky et al., 2003). Therefore, ionizing radiation increases the rate of crosslinking in methylsilicone compared to thermal crosslinking.

The bubble formation indicates that poly-condensation crosslinking mechanisms were activated by radiolysis reactions. The foam structure resulted from the gaseous products which acted as the blowing agent. Because of the active groups of hydroxyl and ethoxy present in a ~4 mol% in the methylsilicone resin the following reactions are expected to occur with the release of water (reaction (2)) and ethanol (reaction (3)) as by-products acting as blowing agent in the molten polymer:

$$\equiv Si\text{–}OH^{\bullet} + {}^{\bullet}HO\text{–}Si \equiv \rightarrow \equiv Si\text{–}O\text{–}Si \equiv + H_2O\uparrow \quad (2)$$

$$\equiv Si\text{–}OC_2H_5^{\bullet} + {}^{\bullet}HO\text{–}Si \equiv \rightarrow \equiv Si\text{–}O\text{–}Si \equiv + C_2H_5OH\uparrow \quad (3)$$

The FTIR analysis of irradiated methylsilicone is shown in Fig. 2. The spectra are exhibited in two graphics, one shows the non-irradiated resin and samples irradiated with 1.0, 3.5, 7.0 and 9.0 MGy (Fig. 2a) and other contains spectra corresponding to samples irradiated with doses of 2.0, 2.5 and 3.0 MGy (Fig. 2b). There are no marked differences in the FTIR spectrum of the

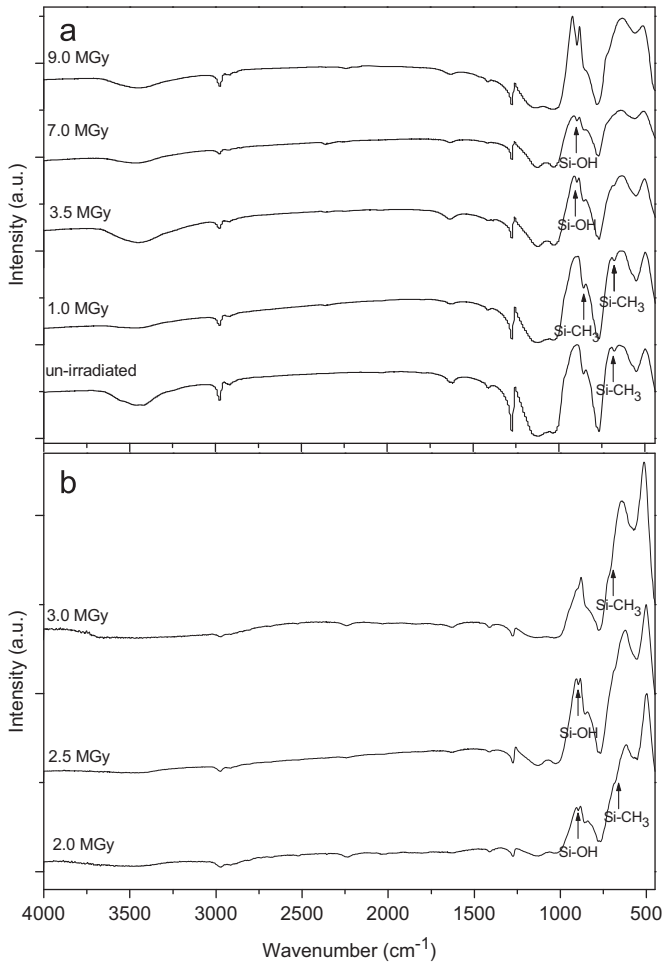

Fig. 2. FTIR spectra: (a) non-irradiated methylsilicone sample and EB irradiated samples with doses of 1.0, 3.5, 7.0 and 9.0 MGy; (b) with doses of 2.0, 2.5 and 3.0 MGy.

non-irradiated and the irradiated methylsilicone with 1.0 MGy. However, it was observed a reduction in the intensity bands of Si–CH_3 stretching (857 and 740 cm^{-1}) and bending (1269 cm^{-1}) of the samples irradiated with curing doses higher than 2.0 MGy. These changes can be attributed to partial transformation of the methyl group during EB irradiation. Since no publications related to irradiation of methylsilicone resin were found to help explain structural modifications, we have used the studies related to irradiation of polydimethylsiloxane (PDMS). PDMS has a linear structure with methyl side groups, whereas methylsilicone resin is a non-linear polymer containing large amounts of oligomeric methyl silsesquioxane ($CH_3SiO_{3/2}$). Irradiation of PDMS in vacuum is known to result in crosslinking based on C–H and C–Si bond scission in the methyl (CH_3) side chain with formation of Si–Si, Si–CH_2–Si and Si–CH_2–CH_2–Si bonds (Miller, 1960 and Charlesby, 1991). Due to these crosslinking reactions in PDMS, volatile products such as hydrogen, methane and ethane are formed during irradiation. However, irradiation of PDMS in presence of oxygen generates CO and CO_2 because of the oxidation of methyl groups (Menhofer et al., 1989). The following sequence of oxidation reactions occurs:

$$Si–CH_3 \rightarrow Si–CHO \rightarrow Si–COOH \quad (4)$$

$$\rightarrow Si–OH+CO \quad (5)$$

$$\rightarrow Si–H+CO_2 \quad (6)$$

The evolution of CO and CO_2 increases markedly with rising irradiation temperature (Menhofer et al., 1989). It is probable that the evolution of these volatile species during EB irradiation also contribute towards bubble formation and expansion of the molten methylsilicone.

FTIR spectra of samples irradiated with doses from 2.0 MGy also showed an additional band at 895 cm^{-1}. This band was attributed to the Si–OH groups and it was also observed by Miller (1961) in the infrared spectrum of irradiated PDMS. He proposed that the appearance of this band was due to main chain scission generating Si–$O^{\bullet}$ radicals with the hydrogen absorbency. This last observation suggests that radiation doses above 2.0 MGy could cause some degradation in the polymer structure due to main chain scission.

The extent of crosslinking in samples irradiated with different radiation doses was evaluated by gel fraction determination. This method was not succeeded to determine the gel fraction of samples irradiated with 1.0 MGy, because none material was retained by the permeable fabric during extraction. This fact can be related to the too low degree of crosslinking with small nucleation points in samples irradiated with 1.0 MGy. This result suggests that the bubble formation observed in samples irradiated with 1.0 MGy is more associated with the oxidation of the CH_3 groups with releasing of CO and CO_2 (reactions (5) and (6)) than the poly-condensation reactions (reactions (2) and (3)) with releasing of water and ethanol. On the other hand, samples irradiated with doses from 2.0 to 9.0 MGy were almost insoluble with gel fractions higher than 95% (Table 1). These results imply that it was created a three-dimensional network structure in the foams irradiated with dose higher than 2.0 MGy that markedly reduced its dissolution. In this way, reactions (2) and (3) are intensified with irradiation dose between 1.0 and 2.0 MGy, promoting overall crosslinking and higher expansion by gaseous species evolution. Therefore, the maximum amount of crosslinking in methylsilicone, when EB radiation is used in air at dose rate of 2.8 kG/s, occurred between 1.0 and 2.0 MGy.

The conversion of methylsilicone foam to SiOC ceramic was studied by thermogravimetry (TG) at temperature up to 1000 °C in air atmosphere (Fig. 3). The foam obtained with dose of 1.0 MGy shows a TG curve typical of a methylsilicone with low degree of crosslinking (Takahashi and Colombo, 2003). This is in agreement with the low bubble formation and the impossibility to measure its gel fraction. The ceramic yield of this sample was about 81%, slightly higher than that of the non-irradiated polymer. The curves of the non-irradiated and the 1.0 MGy irradiated material show that most of the weight change occurred in two steps, located around 200 and 400 °C. Moreover, there was no weight change at 200 °C for foams irradiated with doses of 2.0, 2.5 and 3.5 MGy. These findings indicate that the first weight loss can be attributed to crosslinking reactions with release of gaseous by-products, or to the evaporation of low molecular weight components. The second weight loss can be attributed to the main degradation reactions of methylsilicone, which occur with cleavage of Si-(CH_3) and to oxidation reactions of the methyl groups (Renlund et al.,

Table 1
Gel fraction of the methylsilicone resin irradiated at various radiation doses.

Irradiation dose (MGy)	Reticulation degree (%)
1.0	0
2.0	95.2 ± 1.2
2.5	96.1 ± 0.3
3.0	97.1 ± 0.7
3.5	95.2 ± 0.9
7.0	98.5 ± 0.6
9.0	99.1 ± 0.3

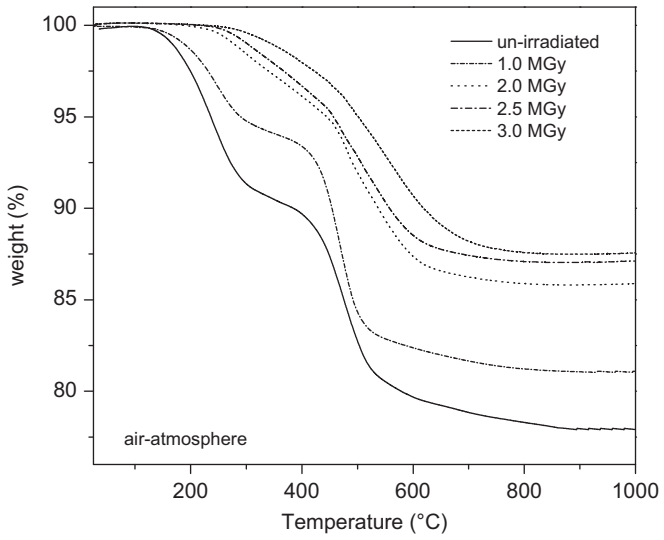

Fig. 3. TGA curves of the non-irradiated methylsilicone and EB irradiated samples with doses of 1.0, 2.0, 2.5 and 3.0 MGy (heating rate of 10 °C/min in air atmosphere).

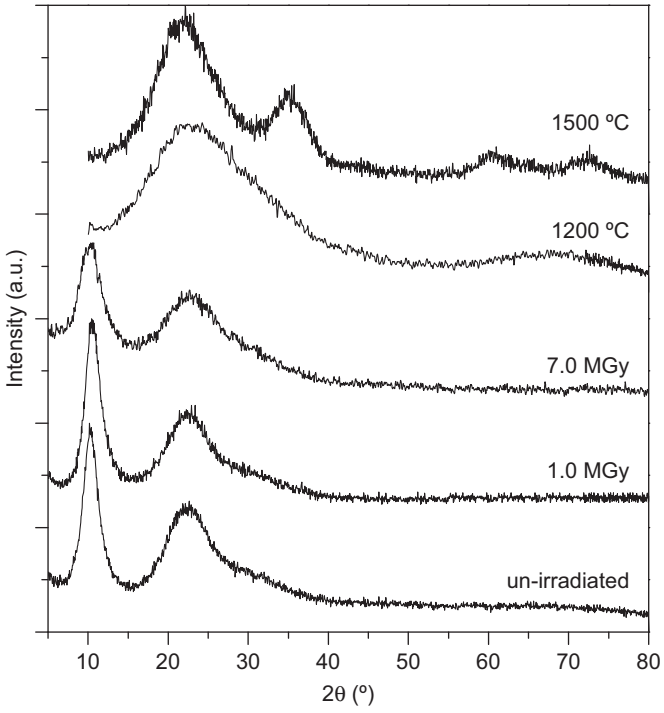

Fig. 4. XRD patterns of the non-irradiated methylsilicone, EB irradiated samples with dose of 1.0 and 7.0 MGy and pyrolyzed samples at 1200 and 1500 °C.

1991). The foam obtained with doses of 2.0, 2.5 and 3.5 MGy showed similar TG curves and small differences in the final ceramic yield, from 85.8% to 87.5%. However, as radiation dose increased the initial weight loss was shifted to higher temperature. This fact can be associated to the increasing oxidative degradation in samples exposure to higher radiation doses, reaching external temperatures of about 260 °C. According to the fabricant, methylsilicone resin withstands continuous temperature up to at least 200 °C or even higher for short periods. At temperatures of 250 °C and above oxidative degradation of the silicon-bound methyl groups occur.

Fig. 4 shows the XRD analysis data of the non-irradiated methylsilicone, after EB irradiation with doses of 1.0 and 7.0 MGy and the pyrolyzed foam at 1200 and 1500 °C. The XRD patterns of un-pyrolyzed samples reveal two peaks, at $2\theta \sim 10^\circ$ and 22°, regardless of the condition of the methylsilicone. The most likely interpretation for the existence of two peaks is that the silicone resins contain an amorphous phase, corresponding to the broad peak around 21° and a relatively regular structure corresponding to the higher intensity peak at 10° (Takahashi et al., 2001). After pyrolysis at 1200 °C the peak considered with regular structure, about $2\theta \sim 21^\circ$ (Fig. 4), was not observed and there is an amorphous pattern attributable to amorphous silicon oxycarbide (SiOC) ceramic, which is typical when siloxane resins are used as pre-ceramic precursors (Renlund et al., 1991). The sample pyrolyzed at 1500 °C shows two broad peaks at 2θ of ~22° and 35° with two main broad halos centered at 2θ at 60° and 72°, which permit precise assignment and to formation of β-SiC nanocrystals (Pantano et al., 1999). A porosity of ~84% was achieved in the pyrolyzed foams, with cell size ranging from 30 to 300 μm and bulk density of about 0.31 g cm^{-3}.

4. Conclusions

Methylsilicone resin was foamed in a single step manufacturing process by electron beam (EB) irradiation. The polymer precursor was expanded by gaseous products that evolved from the methyl group oxidation and condensation crosslinking reactions during irradiation. The required irradiation dose for methylsilicone resin, at dose rate of 2.8 kGy/s, was found to be between 1.0 and 2.0 MGy. The foams obtained with radiation dose from 2.0 MGy exhibited high degree of crosslinking (>95%) and high ceramic yield (>85.5% in air atmosphere). Pyrolysis of the methylsiloxane derived foam in an inert atmosphere led to the formation of amorphous SiOC ceramic foams at 1200 °C, and partly crystalline SiOC at 1500 °C, with large open cells and dense struts. Total porosity was about 84% with bulk density of 0.3 g/cm^3.

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